Synthesis of the Tetrahydrothiopyrano[1,2-*a*]benzothiophenium Ring System by Intramolecular Cyclo-*S*-alkylation

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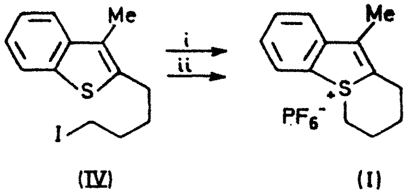
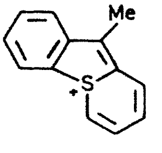
Summary Intramolecular cyclization *via* ring closure at thiophenic sulphur (cyclo-*S*-alkylation) gives the new trigonally bonded bridged sulphonium heterocycle, 6,7,8,9-tetrahydro-10-methylthiopyrano[1,2-*a*]benzothiophenium ion.

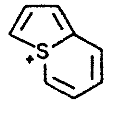
WE report the synthesis of an unusual bridged bicyclic sulphonium ion and novel heterocyclic system, 6,7,8,9-tetrahydro-10-methylthiopyrano[1,2-*a*]benzothiophenium hexafluorophosphate (I). This is the first synthesis of the thiopyrano[1,2-*a*]benzothiophenium ring system and first intramolecular cyclization resulting in ring fusion at the sulphur atom of a thiophenic system.[1] The reaction has potential general applicability in systems containing weakly nucleophilic heteroatoms which can form stable bridged cations. The ion (I) is a precursor and tetrahydro-derivative of the unsaturated bridged cyclic sulphonium ions, thiopyrano[1,2-*a*]benzothiophenium (II), the benzo-derivative of thiopyrano[1,2-*a*]thiophenium (III), our ultimate goal. MO calculations predict exceptional π electron delocalization, perhaps involving sulphur $3d$–$2p$ π interactions.[2]



(IV) (I)



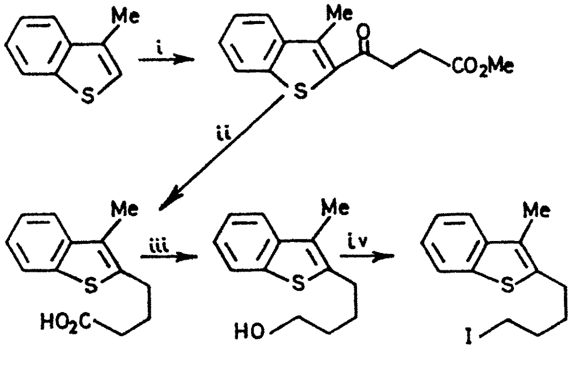
(II)



(III)

Reagents: i $AgPF_6$–$C_2H_4Cl_2$; ii, a $AgClO_4$–C_7H_8; b NH_4PF_6–H_2O.

Ion (I) was approached in two ways: addition of a dilute 1,2-dichloroethane solution of the benzo[*b*]thiophen (IV) to a solution of anhydrous $AgPF_6$ in 1,2-dichloroethane at 0°, or addition of a dilute toluene solution of the iodo-compound (IV) to a toluene solution of anhydrous $AgClO_4$ at 0°, followed by extraction of the precipitated perchlorate with cold water and anion exchange by addition of excess of NH_4PF_6.† The iodo-compound (IV) was prepared from 3-methylbenzo[*b*]thiophen by acylation with β-methoxycarbonylpropionyl chloride followed by Wolff–Kishner reduction of the carbonyl group, $LiAlH_4$-reduction of the carboxylate, tosylation of the alcohol, and displacement by iodide ion.



(IV)

Reagents: i $MeO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$–$SnCl_4$; ii a N_2H_4,H_2O–KOH, diethylene glycol; b HCl–H_2O; iii $LiAlH_4$; iv, a $C_7H_7{\cdot}SO_2Cl$–C_5H_5N; b NaI.

The hexafluorophosphate (I) is white, crystalline (m.p. 130—131°) and gave satisfactory elemental analyses. Comparison of the n.m.r. spectra of the precursor iodo-alkylbenzothiophen (IV) and the tetrahydrothiopyrano-[1,2-*a*]benzothiophenium (I) in SO_2 or $CF_3{\cdot}CO_2H$ showed downfield shifts of the methyl hydrogens from δ 2·1 to 2·5 p.p.m. and the complex aromatic hydrogen absorptions from δ 7·0—7·6 to 7·5—8·2 p.p.m. The saturated ring hydrogens gave very broad complex absorptions.

The observed mass spectrum of (I) (except for the *m/e* 204 and 189 ions) is consistent with that expected for 2-(but-3-enyl)-3-methylbenzo[*b*]thiophen ($C_{13}H_{14}S$ *m/e* 202, 187) (V) which would result from thermally induced pseudo-Hoffman elimination in the probe by loss of a proton β to S^+ in (I) and opening of the saturated ring. Intermolecular hydrogen transfer may also occur as shown by the intensities of the $C_{13}H_{16}S$ (*m/e* 204) and $C_{12}H_{13}S$ (*m/e* 189) ions.‡

The poorly resolved u.v. spectrum of (I) in water was similar to the spectra of (IV) and other 2,3-dialkylbenzo-[*b*]thiophens[3] and to the spectra of authentic 1-methyl- and 1-propyl-benzothiophenium ions. In the 298—301 nm region neutral benzothiophens exhibited a sharp auxiliary

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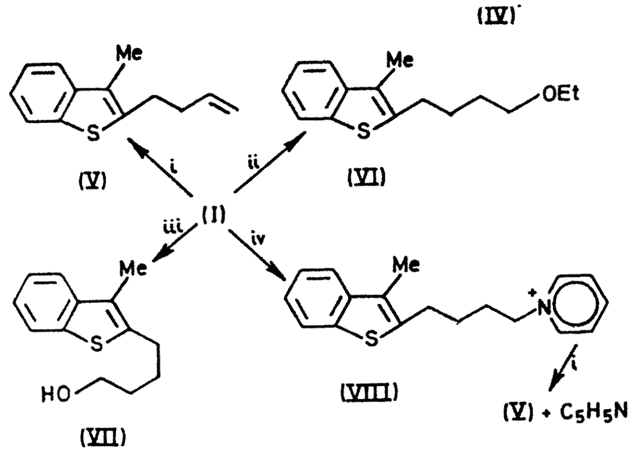
† We have also prepared the tetrafluoroborate salt of (I); the hexafluorophosphate has the most favourable properties for isolation, purity, and stability. An explosion was reported [ref. 1(b)] during a silver perchlorate reaction in which thiophen was reagent and solvent. No such difficulties were encountered in our work, which included syntheses of various thiophenium and benzothiophenium perchlorate salts with excess of toluene as the reaction medium.

‡ The pyrolytic decomposition of *S*-alkylthiophen ions is currently being investigated.

shoulder not present in the benzothiophenium u.v. spectra. Upon repeated scanning of the spectrum of (I) in ethanol rapid appearance and growth of that band (298—301 nm) indicated that solvolysis of the ion (I) was occurring causing ring opening and generation of the benzo[*b*]thiophen (VI). Similar hydrolytic ring opening in water to give the benzothienylbutanol (VII) was also observed but at a slower rate.



Reagents: i heat; ii EtOH; iii H_2O; iv C_5H_5N.

The rapid mildly exothermic reaction of (I) in pyridine gave the ring-opened pyridinium salt (VIII). The structure was assigned on the basis of its n.m.r. spectrum: δ 2·1 (s, Ar*Me*) 4·2 (t), 2·6 (t), and 1·8 (m) (aliphatic), 6·9br (benzo[*b*]thiophen), and 7·9br (pyridinium) p.p.m. The mass spectrum of (VIII) is consistent with formation of pyridine and the but-3-enyl-benzo[*b*]thiophen (V) from thermal Hoffman elimination in the probe.

Dehydrogenation of (I) and other approaches to (II) and other derivatives of thiopyrano[1,2-*a*]thiophenium (III) are currently under investigation.

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[1] (a) The first example of an *S*-alkylthiophen, the *S*-methyl thiophenium ion was reported by G. C. Brumlick, A. I. Kosak, and T. Pitcher, *J. Amer. Chem. Soc.*, 1967, **89**, 3191. (b) R. M. Acheson and D. C. Harrison, *Chem. Comm.*, 1969, **724**, reported syntheses of some *S*-alkylbenzothiophens.

[3] These and related bridged trigonal sulphonium ions are referred to as 'cyclothiolia' by R. Zaradnik in *Adv. Heterocyclic Chem.*, 1965, **5**, 38.

[3] E. G. G. Werner, *Rec. Trav. Chem.*, 1949, **68**, 509.